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Introduction

This chapter presents the outline of thin film technologies currently used and describes the relationship among catalytic chemical vapor deposition (Cat-CVD) and other conventional thin film technologies. In this chapter, the history of Cat-CVD and its related technologies is also briefly reviewed. Finally, the structure of this book is explained for easier reading.

1.1 Thin Film Technologies

Most industrial consumer products are coated with various thin films. Some products may be covered by painting or plating films. Thin film coating is also seen in modern electronic products. In such cases, quite often, the quality of the coating films determines the performance of the electronic products themselves. For instance, in liquid crystal displays (LCDs) or organic electroluminescent displays, transistors made of semiconductor thin films are working as a key device to control the brightness and colors of pictures. In ultralarge-scale integrated circuits (ULSI), used in computers as a key device, many thin films are contained, and the quality of such thin films strongly determines the performance of ULSI. In solar cells, the quality of thin films also determines their energy conversion efficiency.

So far, many thin film technologies have been invented. Coating technology on various tools was invented at least more than 10 000 years ago. It is well known that the painted drawing on the walls of stone caves can have a history of more than 40 000 years.

Here, let us depict a family tree of thin film technologies. It is very useful to make a family tree of related research for taking a view point of our own research in the tree to judge the value of the research itself. It can sometimes lead to new ideas and helps to define what we should do in future for our own technology from a deeper understanding of the position of research. The family tree is shown in Figure 1.1. It demonstrates that the thin film technologies are divided to three major technologies.

The first one is the pasting of thin films on solid substrates, where such thin films are prepared elsewhere. As a historical technology, pasting of gold leaf on solids is known. Because gold bullion can be stretched and transformed to a sheet

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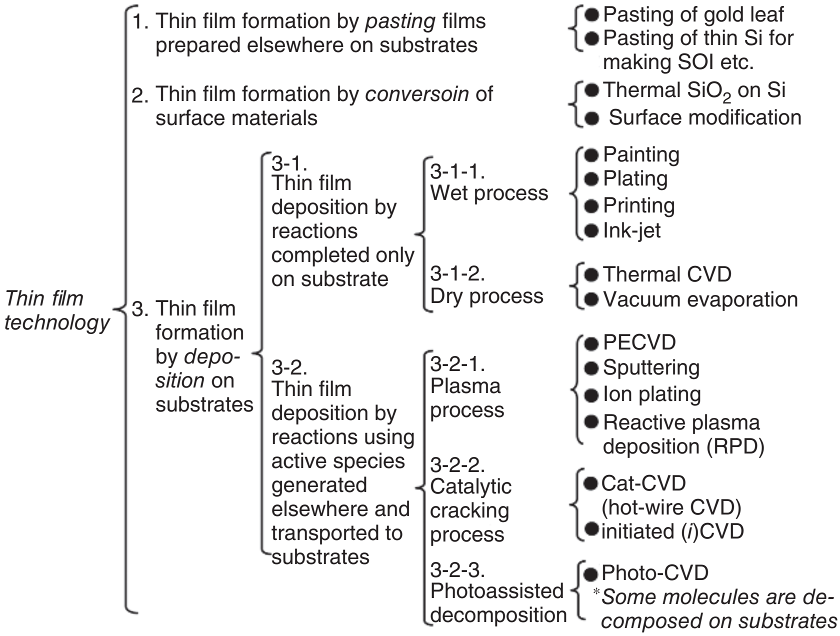

Figure 1.1 A family tree of thin film technologies. SOI and PECVD are abbreviations of silicon on insulator and plasma-enhanced chemical vapor deposition, respectively.

by beating, a thin gold leaf with a thickness less than 100 nm can be made and attached strongly on the surface of solids. The second is the formation of thin films by converting the thin surface layer of a solid to a layer of different materials by chemical reactions of the solid surface with active gases. For instance, the thermal oxidation of crystalline silicon (c-Si) wafers to form a silicon dioxide (SiO_2) layer at the surface is a widely spread technique within this category. The third is the formation of thin films by deposition on solid substrates. Films are formed at the surface of substrates by deposition of species supplied from outside of the substrate. This technology is divided into two groups: one is the method in which the film forming process is completed on the surface of substrates and the other is the method in which molecules are decomposed in advance remotely from the substrates, and such activated species are used in the reactions of film formation at the surface of substrates. Usually, by using species activated in advance, the high-quality films can be obtained at relatively low substrate temperatures, typically lower than 300 °C.

The methods utilizing activated species created outside of the substrates are further divided into three groups. One of the methods uses plasma for the generation of active species, the second method uses catalytic cracking reactions, and the third one uses the energy of radiation, such as photochemical vapor deposition (Photo-CVD). In Photo-CVD, there is discussion on the possibility of direct excitation of adsorbed molecules on the surface of substrates rather than in the gas phase outside of substrates. In this case, the method fits better in the group of 3-1-2.

Plasma-enhanced chemical vapor deposition (PECVD) is the first method, in which molecules of source gases are decomposed by the collisions with energetic electrons generated in plasma. The method using catalytic cracking reactions to decompose molecules is Cat-CVD. In Cat-CVD, as heated metal wires are usually used, the method is often called hot-wire CVD or hot filament CVD. In Cat-CVD, no plasma is needed.

A similar technology using heated metal wires is known as initiated chemical vapor deposition (*i*CVD). In this newly developed method, activation of initiators is due to heated metal wires, and the activated species are inducing polymerization of adsorbed monomers at the surface of substrates, resulting in high-quality organic thin films. This method is suitable for the preparation of device quality organic polymer films.

Looking at the family tree, one may notice that there is plenty of spaces for the first divided groups in which the films are prepared in advance, outside of the substrates. For instance, in the family tree of creatures, at first, the creatures are divided into plants and animals, and there is a roughly equal number of branches in the two groups. However, in the case of the family tree of thin film technology, the first and second divided groups do not have as many branches or methods compared with the third method of thin film deposition. This means that there is a big potential to invent new thin film technologies in the first and second groups. For instance, if patterned thin films, made apart from the substrates, are pasted on substrates, the thin film formation process becomes much more cost effective. The prototype of this idea is already seen commercially for pasting painted sheets on walls of air planes, trains, and buses for advertisement. If thin films are more sophisticated, this idea will be used in industrial electronic devices, in particular, large area devices. By looking at the family tree, you can enjoy more to create new ideas.

1.2 Birth of Cat-CVD

Catalytic cracking is a well-known phenomenon. It was already known in the 1910s that hydrogen (H) atoms are simply generated by catalytic cracking reactions of a hydrogen molecule (H_2) with heated tungsten (W) wires [1]. Since the 1970s, H. Matsumura et al. concentrated on making high-quality and thermally stable amorphous silicon (a-Si) films by using fluorine (F) atoms as dangling bond terminators. Particularly, they used silicon difluoride (SiF_2) molecules as a source for the formation of fluorinated a-Si (a-Si:F) films. By using SiF_2, such a-Si:F films were formed by simple plasma-less thermal CVD, although the quality of the films was slightly less than that of hydrogenated a-Si (a-Si:H) films prepared by PECVD. Thus, to improve film quality, Matsumura attempted to introduce H atoms into such a-Si:F films. As the films were obtained without the use of plasma, he pursued the use of H atoms created by catalytic cracking reaction of H_2 molecules at heated W wires to complete the development of a plasma damage-free deposition system. The work had been carried out from 1983 to 1985. The result was very encouraging. The property of such films appeared better than those of PECVD a-Si:H films. Matsumura named the method “Cat-CVD” in 1985.

The film quality was excellent; however, the results could not make the industry adopt this method, as they would not add halogen gases to their system because their systems preparing a-Si:H films had just been constructed in many companies. Then, he attempted to deposit a-Si:H by cracking of silane (SiH_4) gas with heated W wires and succeeded in obtaining device quality a-Si:H films in the period from 1985 to 1986. This makes the birth of Cat-CVD technology. Matsumura succeeded in obtaining device quality a-Si films without the assistance of plasmas for the first time.

1.3 Research History of Cat-CVD and Related Technologies

The combination of thermal CVD with catalysis of metals was first reported in 1970 by S. Yamazaki et al. at Doshisha University, Japan. He installed catalysts such as platinum and nickel oxide just near the substrates in a quartz tube of a conventional atmospheric pressure thermal CVD apparatus for preparing silicon nitride (SiN_x) films [2]. This catalyzer was just put near the substrates and it was unheated. He discovered that the temperature for forming SiN_x films on the substrates could be reduced from 700 to 600 °C by the effect of the presence of catalysts nearby. The role of catalysts and the mechanism for lowering the deposition temperature were not clearly explained in the report. This also did not show the invention of a low pressure and low temperature deposition method, although metal wires were used as an example of catalysis.

Later, in 1979, H. Wiesmann et al., at the Brookhaven National Laboratory, USA, reported their discovery that a-Si films could be formed when heated W wires and carbon foils were exposed to silane (SiH_4) gas in a low-pressure chamber [3]. This is the first report on the discovery of a-Si formation using heated W wires. However, as the quality of the a-Si films was less than that of PECVD a-Si:H and therefore the method appeared non-attractive, this work did not collect much attention and had been forgotten for several years until the work of Cat-CVD by Matsumura was reported. In addition, as they believed that the process for the decomposition of SiH_4 molecules was simply pyrolytic, the work did not lead to further understanding of the deposition mechanism based on catalytic reactions on the surface of metals.

In 1982, S. Matsumoto et al., at the National Institute for Research in Inorganic Materials, Japan, reported that diamond-like carbons (DLCs) could be obtained from methane (CH_4) gas when substrates were put in a conventional high-temperature thermal CVD chamber at temperatures between 800 and 1000 °C [4]. The substrates were heated further by heated W wires placed near them. At that time, the role of W wires was not clear, except for the role of additional heating of the substrates. Although they attempted to lower the temperatures later, this did not lead to the invention of a low-temperature deposition system at that time. Later, there were a number of reports discussing the role of W wires. In 1985, A. Sawabe and T. Inuzaka at Aoyama Gakuin University, Japan, reported the effect of electrons emitted from heated W wires on the growth of carbon films to enhance the crystallization of DLC films [5].

In 1985 and 1986, Matsumura et al. at the University of Hiroshima, Japan (later he moved to JAIST), reported the success of obtaining device quality hydrofluorinated a-Si (a-Si:F:H) [6, 7] and a-Si:H [8] at low temperatures, and they presented the concept of catalytic cracking playing a major role in the decomposition of material gases. In 1987, Matsumura also succeeded in making device quality amorphous silicon–germanium (a-SiGe) films [9] and in 1989, he also succeeded in obtaining device quality SiN_x films [10]. The success of formation of SiN_x films by Cat-CVD was also reported by K. Yasui et al., at the Nagaoka University of Technology, Japan, in 1990 [11]. In their case, they used SiH_4 and mono-methylamine as source gases and also used a W filament heated at 2400 °C.

Matsumura continued the research of Cat-CVD, and in 1991, he succeeded in obtaining even polycrystalline Si (poly-Si) or microcrystalline silicon (μc-Si) by adjusting the deposition parameters from those used in a-Si formation to mixture of SiH_4 with a large amount of H_2 [12]. In addition, these successes encouragingly demonstrated the big feasibility of this method as a new thin film technology.

After the success of preparation of a-SiGe, in 1988, Doyle et al. at Colorado University, USA, demonstrated the results of further advanced studies on Cat-CVD a-Si films by showing the feasibility to obtain a-Si films with excellent properties, although they named the method "evaporative surface decomposition (ESD)" [13].

In 1991, A.H. Mahan et al., at Solar Energy Research Institute (SERI, presently, National Renewable Energy Laboratories, NREL), USA, reported, by detailed comparison of two deposition methods, the superiority of Cat-CVD a-Si to that deposited by PECVD, although they named the method at that time "hot-wire CVD" [14]. Their scientifically well-elaborated reports contributed to the wide expansion of Cat-CVD-related research in the world. Since then, the number of researchers working on Cat-CVD or hot-wire CVD has increased.

Actually, in 1992, J. L. Dupuie and E. Gulari, University of Michigan, USA, reported the success of obtaining high-quality aluminum nitride (AlN) films by Cat-CVD using ammonia (NH_3) and trimethylaluminum (TMA) with a W catalyzer heated at about 1750 °C [15]. In addition, in 1992, J. L. Dupuie et al. also succeeded in confirming the formation of device quality SiN_x films by using Cat-CVD technology [16].

There have been many reports on various examples of application of Cat-CVD a-Si films and SiN_x films in the 1990s to 2000s. For instance, in 1995, R. Hattori et al. succeeded in obtaining high-quality SiN_x coating films for gallium–arsenide (GaAs) high-frequency transistors by using Cat-CVD and reported the superiority of device performance of GaAs transistors using Cat-CVD films to that using PECVD films [17]. In 1997, R.E.I. Schropp et al. succeeded in preparing state-of-the-art solar cells [18] and thin film transistors (TFTs) [19]. They also succeeded in preparing SiN_x films used as passivation films [20], gate dielectrics [21], and chemical barrier films [22] for various devices.

Concerned with the application to solar cells, there are also many reports from the NREL group. The progress of their group was summarized in Ref. [23]. For instance, in 1993, at first, E. Iwaniczko and coworkers succeeded in fabricating p-i-n a-Si solar cells by using i-a-Si layer prepared by Cat-CVD with a deposition rate of 0.9 nm/s. The deposition rate was very fast, compared with PECVD a-Si at that time. After various efforts, in 1998, A.H. Mahan et al. succeeded in obtaining full Cat-CVD p-i-n a-Si solar cells with an efficiency of 9.8%, at a deposition rate of 1.6 nm/s for the i-layer. The deposition rate was improved to 1.8 nm/s keeping the efficiency at 9.8% in 1999 by Q. Wang and coworkers.

Apart from these movements, many research studies on Cat-CVD a-Si and microcrystalline silicon (μc-Si), which includes crystallites in a-Si, had been carried out by the group of B. Schroeder et al. at the University of Kaiserslautern, Germany [24], by the group of J.E. Bouree and coworkers at Ecole Polytechnique, France [25], and some other groups.

Apart from these applications to electronic devices, from the middle of 1990s, chemistry groups mainly led by K.K. Gleason and coworkers at the Massachusetts Institute of Technology (MIT), USA, started to use this CVD technology using heated filaments for the formation of completely different materials such as polymer films and also started to think of applications, although they did not use the term "Cat-CVD" because there was no verification of catalytic reactions in their systems at that time. Probably, the research might be encouraged by the work of DLC films using a hot metal filament, as they like to use the term of "hot filament CVD" in the initial stage.

In 1996, S.J. Limb et al. of K. Gleason's group reported the success of obtaining polytetrafluoroethylene (PTFE, widely known by its commercial name "Teflon") films by using hexafluoropropylene oxide (HFPO) gas and heated nickel–chrome (NiCr) wires [26]. The temperature of the NiCr wires was about 325 to 535 °C, much lower than that of the W catalyzer during deposition of a-Si films. They revealed the superior property of PTFE films prepared by their hot filament CVD.

In 2001, H.G. Pryce Lewis et al., belonging to the same group, discovered and reported that the deposition rates of such PTFE films could be easily increased from 40 to 1000 nm/min, for instance, by adding perfluorooctane sulfonyl fluoride (PFOSF, $CF_3(CF_2)_7SO_2F$) gas as an initiator of reactions to HFPO as the source gas [27]. Since then, they had started to study on the mechanism of organic film formation and the role of an initiator. Finally, they reached a conclusion on the film formation process, revealing the importance of the selection of a proper initiator, and named the method "initiated chemical vapor deposition (*i*CVD)" in 2005 [28].

According to their explanation, in *i*CVD, at first, vapors of a monomer and an initiator are fed into the vacuum CVD chamber, and secondly, the initiator is activated in the gas phase in the hot zone near the heated filament. They claim that the activation is carried out by the heat transferred from the filament rather than by catalytic cracking. Subsequently, the monomer and the activated initiator are adsorbed on cooled substrates near to room temperature, and finally, polymerization starts on the surface of the substrates and growth of polymer films is started.

As the temperature of the filament in *i*CVD is usually kept below 500 °C, which is below the temperature for CH_3 decomposition, the filament metal is not carburized (carbided), and thus, the filament can be used for a very long time. Also, in *i*CVD, as gas phase reactions are important, the gas pressure during deposition is usually much higher than that in Cat-CVD.

Although the apparatus of *i*CVD is quite similar to that of Cat-CVD, the deposition mechanism may be markedly different, and so, they used a different name for their deposition method. As a new synthesizing method of high-quality organic polymer, further progress of the *i*CVD research is expected.

In this book, the deposition mechanism of Cat-CVD (hot-wire CVD) is explained in detail, and in addition, *i*CVD and its application are briefly introduced.

1.4 Structure of This Book

This book aims to present comprehensive overviews of all CVD methods using heated filaments, such as Cat-CVD technologies. It includes fundamental physics of vacuum and molecular dynamics in the vacuum chambers to provide easier understanding of the relevant background to the reader. It also includes a brief explanation of the conventional PECVD method, to compare it with Cat-CVD and understand the difference from Cat-CVD. An analysis of chemical reactions is given in detail, as this is a key to understand the deposition mechanism of Cat-CVD. This, particularly in relation to CVD using heated filaments, has not been systematically described in any other book as far as the authors know. The explanation is put forward as simple as possible, for easier understanding.

Fundamental physics and fundamental processing concepts of Cat-CVD are explained in Chapter 2, along with the explanation of the differences from PECVD, after first describing the features of PECVD. The detailed explanation of various radical detection techniques, which reveal the deposition mechanism of Cat-CVD, is described in Chapter 3. In Chapter 4, the deposition mechanism and chemical reactions in Cat-CVD are described based on the experimental results.

In Chapter 5, the properties of inorganic films prepared by Cat-CVD are mentioned. In this chapter, the meaning of physical parameters that are obtained in Cat-CVD films is explained, particularly for a-Si as a typical example of amorphous materials. The film formation process is explained by using various models. To explain the phenomena in a straightforward manner, the model is considerably simplified. Obviously, this does require sacrificing a detailed and accurate explanation, for which we refer to dedicated publications.

In Chapter 6, the preparation of organic films, based on processes similar to Cat-CVD, is presented. Particularly, *i*CVD and its application are explained.

In Chapter 7, the physics used for designing a Cat-CVD apparatus is elaborated. Gas flow, the factors deciding film uniformity, the effect of thermal radiation from the heated catalyzer, as well as methods to suppress it, and the key points for designing mass production machines are explained and discussed. The issue of contamination released from the heated wires and methods for chamber cleaning are also discussed. The lifetime of catalyzing wires is one of the challenges in Cat-CVD. This topic is dealt with in this chapter, along with various possible methods for extension of the lifetimes of catalyzing wires.

In Chapter 8, various applications of Cat-CVD technologies are introduced. A broad variety of applications have been developed.

In Chapters 9 and 10, the radical species generated in the Cat-CVD apparatus, the properties, and the applications of such radicals are summarized. Particularly, in Chapter 10, a new impurity doping technology, named "Cat-doping," is introduced. In this new technology, boron and phosphorus atoms are introduced into crystalline silicon at temperatures as low as 80 °C and demonstrated to be active dopants.

Throughout this book, the reader will appreciate that CVD using heated filaments, such as Cat-CVD and related technologies, has a promising future.

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